Induced infrared absorption in gaseous acetylene at pressure

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INDUCED INFRARED ABSORPTION IN GASEOUS ACETYLENE AT PRESSURE*

By Shigeru Minomura

Introduction

The infrared absorption spectra of gases at pressure show significant differences in both the frequency of the band maximum and in the probability of the transition from the spectra of gases in the neighbourhood of atmospheric pressure. H. L. Welsh *et al.*[1] have observed that the vibrations of homonuclear diatomic molecules (oxygen, nitrogen, and hydrogen) and the symmetrical vibration of carbon dioxide, normally inactive in infrared absorption, are active in gases at pressure. Such pressure-induced absorption is caused by the distortion of the electronic charge distribution of the molecules in the course of collision.

On the other hand, E. B. Wilson and A. J. Wells[2] have shown that it should be possible under proper conditions to obtain the values of the intensities of an infrared vibrational absorption band by measuring the integrated apparent absorption coefficient for unit pressure at a series of partial pressures of the absorbing gas and extrapolating this quantity to zero partial pressure, and that the rotational fine structure should be eliminated by some suitable non-absorbing gas at sufficiently high pressure. The effect of pressure of non-absorbing gas on an infrared absorption band has been observed by H. L. Welsh *et al.*[3] for gaseous methane up to 600 atm and by S. S. Penner and D. Weber[4] for gaseous carbon monoxide up to 700 psia, and it has been shown to yield a more reliable estimate of the intensity of the band that the pressure of the foreign gas should be extended to large values and the pressure broadening of the rotational lines very great. That is, the integrated absolute absorption coefficient of the free absorbing gas should be estimated by measuring the variation

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* *Part of this investigation was published by R. Kiyama, S. Minomura and K. Ozawa in Proc. Japan Acad.*, **30** 758 (1954) (*Communicated by S. Horiba, M. J. A., Oct.* 12, 1954)

1) M. F. Crawford, H. L. Welsh and J. L. Locke, *Phys. Rev.*, **75**, 1607 (1949); **76**, 580 (1949)
M. F. Crawford, H. L. Welsh, J. C. F. MacDonald and J. L. Locke, *ibid.*, **80**, 469 (1950)
D. A. Chisholm and H. L. Welsh, *Can. J. Phys.*, **32**, 291 (1954)

2) E. B. Wilson and A. J. Wells, *J. Chem. Phys.*, **14**, 578 (1946)
A. M. Thorndike, A. J. Wells and E. B. Willson, *ibid.*, **15**, 157 (1947)
A. M. Thorndike, *ibid.*, **15**, 868 (1947)

3) H. L. Welsh, P. E. Pashler and A. F. Dunn, *ibid.*, **19**, 340 (1951)

4) S. S. Penner and D. Weber, *ibid.*, **19**, 807, 817, 1351 (1951)

of the integrated absolute absorption coefficient in the gaseous mixture with the Amagat density of the foreign gas and by extrapolating the linear portion of the variation curve to zero density of the foreign gas.

The author has observed the infrared absorption in gaseous acetylene at pressures up to 24 kg/cm² over the frequency range of 1100~5800 cm^{-1} at room temperature of 23~25°C, and found the pressure-induced absorption band which located at the frequency (1974 cm^{-1}) of the symmetrical vibration (ν_2), normally inactive in infrared absorption. At the same time the influence of oxygen at pressures up to 20 kg/cm² on the apparent intensity of the band at 1328 cm^{-1} ($\nu_4+\nu_5$) of acetylene at several partial pressures over 1~126 mmHg has been measured, and it has been found that the integrated absolute absorption coefficient in the mixtures of acetylene and oxygen increases with the density of oxygen. All the experimental features are attributed to the dipole moment induced by intermolecular forces in the course of collision.

Experimentals

Preparation of acetylene and oxygen The gaseous acetylene from calcium carbide and water was passed through a dry refining reagent* and preserved in gas holder. The gas was bubbled in 30~40 per cent aqueous solution of potassium hydroxide and compressed at a desired pressure. The purity of acetylene was determined with bromine water to be 99.6 per cent. Compressed oxygen of the purity of 99.5 per cent was taken from a commercial bomb.

Apparatus Two windows of the same design were set in the symmetrical positions of both sides of the absorption cell and the cell was arranged between the light source and the slit of the spectrometer in order to transmit the light. The total length of the cell was 268 mm. The principal feature of a window is shown in Fig. 1. The path length of the cell (A) was 158~165 mm and the inner diameter 24 mm. Potassium chloride of 24 mm in diameter and 10~16 mm in thickness, being cut from a large single crystal, was used as the window (B). It was designed by the principle of a packingless window, but a cement was used to seal

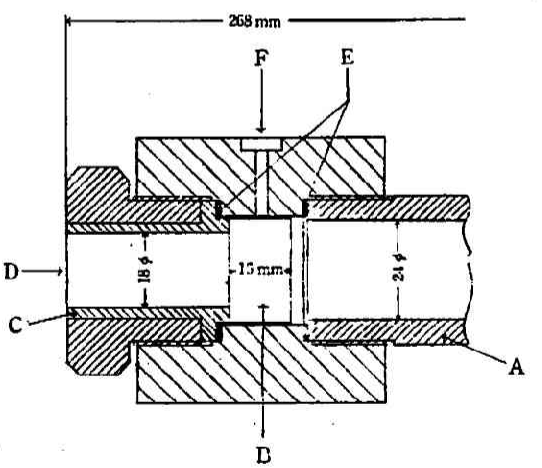

Fig. 1 The diagram of a window of an infrared absorption cell for high pressure gas
A, absorption cell; B, KCl window;
C, window plug; D, observation hole:
E, O-rings; F, Bourdon tube gauge or valves for evacuation and compression of gas

* The refining reagent was a dry mixture of $FeCl_3$, $HgCl_2$, copper acetate and acid clay.

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between the polished surfaces of the window and its supporting plug (C). The diameter of the free area of the window (D) for admitting the transmission of light was 18 mm. O-rings (E) were made of fiber. The Bourdon tube gauge for measuring the pressure of gases in the cell or the valves for evacuation or compression of gases were linked at the part of (F). The result[5] of the experiment on the strength of the optical window of potassium chloride with an observation hole of 4 mm in diameter of the same design has shown no change for 25 hours up to 250 kg/cm², although the apparent elastic limit of potassium chloride has been cited as 2.3×10^7 dyne/cm² in the literature.[6] In the author's experiment which was performed at the gaseous pressure at 24 kg/cm² for several hours the visible plastic deformation[5] and the fracture of the window did not occur. Two absorption cells of the same type were prepared and one of them was used as the reference absorption cell. The decrease of the light transmission of the window with water vapour in the air of the relative humidity below 50 per cent and in the measuring gases was within a few per cent in the experiment over 2 weeks.

Hilger D. 42 Infrared Spectrometer with a NaCl prism and the Nernst lamp as the light source were used for the spectral measurement.

Procedure Two absorption cells were evacuated and in the reference cell was sealed oxygen at 1 kg/cm² and in the other cell was sealed the measuring gases, which were gaseous acetylene at 24, 18, 12, 6, and 1 kg/cm², and acetylene at several partial pressures over 1~126 mmHg pressurized with oxygen at 1, 2, and 20 kg/cm². Readings of the absorption $\log_{10}(T_r/T)$, where T_r is the apparent intensity of light transmitted through the reference cell and T is the apparent intensity of light transmitted through the measuring gases, was taken at the wavelength 0.1 μ apart over the frequency range of 1100~5800 cm^{-1} for acetylene and over 1100~1600 cm^{-1} for mixtures of acetylene and oxygen. The absorption spectra for acetylene were determined by subtracting the absorption in oxygen at 1 kg/cm² as the back ground (T_0), and those for mixtures of acetylene and oxygen were determined by subtracting the absorption in oxygen at the same pressure as the total pressure.

The mixing of gases at pressure takes place very slowly. It was found that significant concentration gradients existed over long periods of time in gases sealed in the absorption cell. In practice, the spectral measurement was performed in 3 hours after the end of mixing of gases and the readings of absorption were reproduced after the lapse of an hour.

Results

The absorption spectra of gaseous acetylene at 24, 18, 12, 6, and 1 kg/cm² are shown in Fig. 2. The spectra indicate the pressure-induced band at 1974 cm^{-1}. If these absorp-

5) R. Kiyama and K. Inoue, *This Journal*, 21, 78 (1951)
6) L. S. Combes, S. S. Ballard and K. A. McCarthy, *J. Opt. Soc. Am.*, 41, 215 (1951)

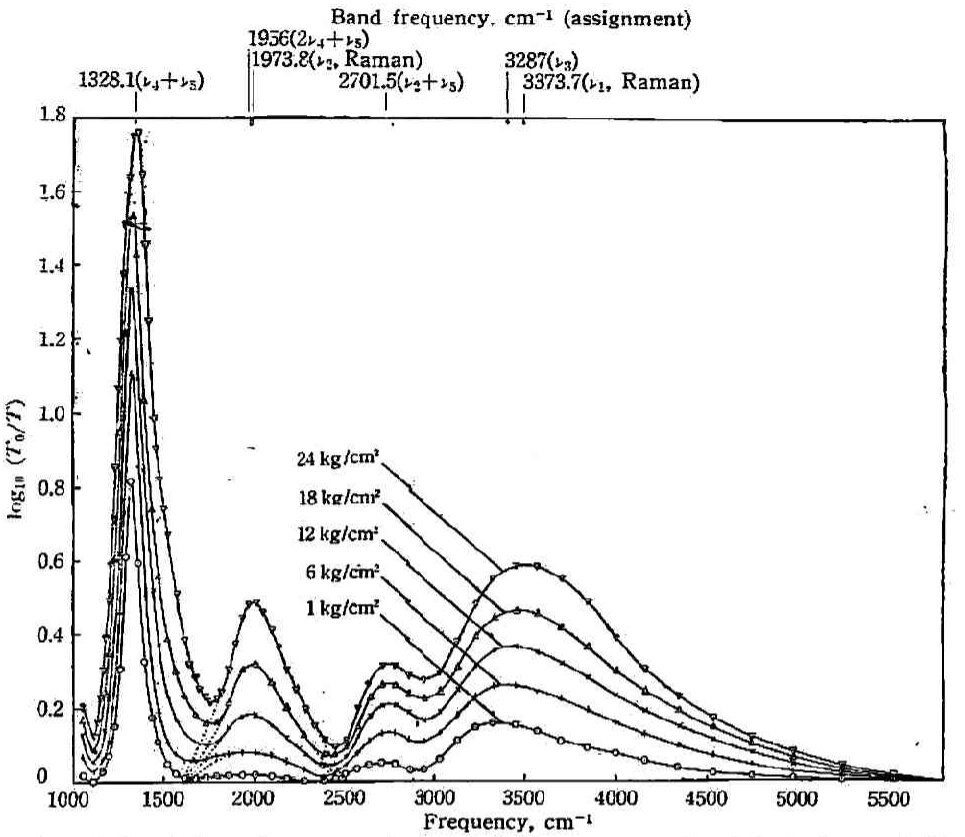

Fig. 2 Infrared absorption spectra of gaseous C_2H_2 at pressures of 1~24 kg/cm² at 23~25°C

tion contours can be given by the dotted lines in the figure, the integrated absorption coefficient of the band for unit Amagat density of acetylene $\frac{1}{\rho l}\int \ln(T_0/T)d\nu$ (in units of frequency ν, cm^{-1}, per path length l, cm, per Amagat density of acetylene ρ) increases proportionally to the Amagat density as shown in Fig. 3. Fig. 4 shows the ratios of the maximum absorption at 1328.1 cm^{-1} ($\nu_4+\nu_5$), 1974 cm^{-1} (pressure-induced band), 2701.5 cm^{-1} ($\nu_2+\nu_5$), and 3287~3500 cm^{-1} (ν_3 and another pressure-induced band) between gaseous acetylene at pressures and at 1 kg/cm², $\log_{10}(T_0/T)_\rho^{max}/\log_{10}(T_0/T)_1^{max}$, against the Amagat density of acetylene. The rate of enhancement of the maximum absorption at 1974 cm^{-1} is remarkably higher than the rates at the other frequencies, and the slope

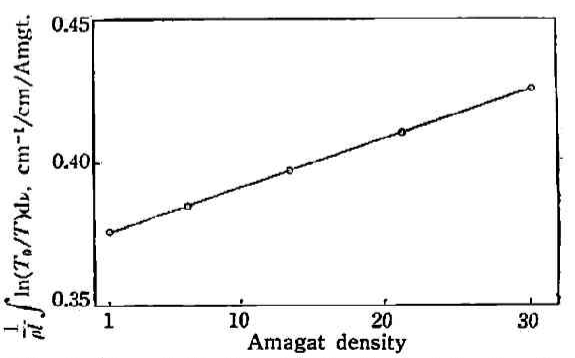

Fig. 3 The relation between the Amagat density of C_2H_2 and the integrated absorption coefficient of 1974 cm^{-1} band for unit Amagat density $\frac{1}{\rho l}\int \ln(T_0/T)d\nu$ (cm^{-1}/cm/Amgt. C_2H_2)

of the curve for 1974cm^{-1} increases with the Amagat density. The variation of the integrated absorption coefficient $\frac{1}{l}\int \ln(T_0/T)d\nu$ (in units of frequency ν, cm^{-1}, per path length l, cm) over the frequency range of 1100~5800cm^{-1} with the Amagat density of acetylene is plotted in Fig. 5, and the slope of the curve decreases slightly with the increase of the Amagat density.

In order to ascertain the influence of pressures (1, 2, and 20kg/cm^2 of oxygen on the absorption band at 1328.1 cm^{-1} of acetylene at several partial pressures over 1~126mmHg, the quantity $\int \ln(T_0/T)d\nu$ (in units of frequency ν, cm^{-1}) is plotted as the function of pl of acetylene (product of partial pressure of acetylene p, cmHg, and path length l, cm) in Fig. 6. The curvature in the curve decreases and the limiting slope of the curve which can be estimated by the extrapolation to zero partial pressure of acetylene, corresponding to the integrated absolute absorption coefficient of the absorption band at 1328.1 cm^{-1} in mixtures of acetylene and oxygen, increases with the increase of the density of oxygen.

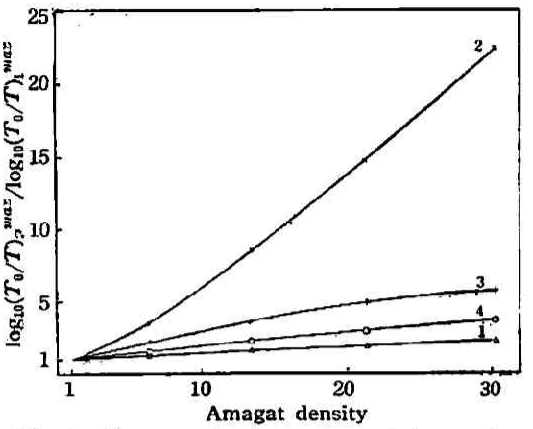

Fig. 4 The rate of enhancement of the maximum absorption at 1328.1cm^{-1} (curve 1), 1974cm^{-1} (curve 2), 2701.5cm^{-1} (curve 3), and 3287~3500cm^{-1} (curve 4) with Amagat density of C_2H_2

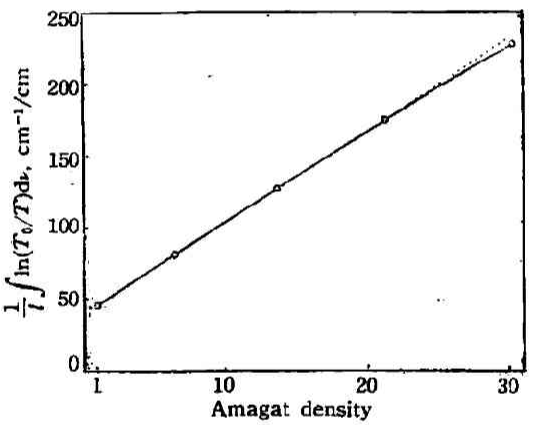

Fig. 5 The relation between the Amagat density of C_2H_2 and the integrated absorption coefficient $\frac{1}{l}\int \ln(T_0/T)d\nu$ (cm^{-1}/cm) over the frequency range of 1100—5800cm^{-1}

Consideration

Acetyene is a molecule of linear and symmetrical type which is expressed by the constitutional formula H—C≡C—H, and the infrared and Raman spectra, which are assigned by the fundamentals of ν_{1-5} and by their combinations, have been observed for acetylene in the neighbourhood of the atmospheric pressure as shown in the following Table.[7]

7) G. Herzberg, *Molecular Spectra and Molecular Structure* (D. Van Nostrand Co., Inc., 1945), p. 288

The fact that the integrated absorption coefficient of the pressure-induced band at 1974cm^{-1} for unit Amagat density of acetylene increases proportionally to the density (Fig. 3) is ascribed to that the intermolecular forces induce the dipole in the course of collision, which arises from the distortion of the electronic charge distribution of molecules. Such proportional relation coincides with the observation by H. L. Welsh *et al.*[1] for the pressure-induced band of homonuclear diatomic molecules at low Amagat density. G. Glockler and C. E. Morrel[8] have observed a very strong Raman band at 1973.8 cm^{-1} which is assigned as ν_2 for liquid acetylene at a pressure of about 895 mmHg at −82°C. As the pressure-induced band locates at the frequency (1974cm^{-1}) of the Raman band, and the rate of enhancement of the maximum absorption at 1974 cm^{-1} is very large in comparison with the rates for the infrared active bands at the other frequencies(Fig. 4), the pressure induced absorption at 1974 cm^{-1} would be caused by the distortion of the symmetrical vibration of the very strong Raman band (ν_2). A weak absorption band at 1956 cm^{-1} which is assigned as $2\nu_4+\nu_5$ has been found by F. Stitt[9] for gaseous acetylene at a pressure of 250 mmHg. As the proportional relation between the integrated absorption coefficient for unit Amagat density and the density does not exist in the other infared active bands, the pressure-induced band at 1974cm^{-1} is not attributed to the pressure broadening of the rotational structure in the combination band at 1956cm^{-1}.

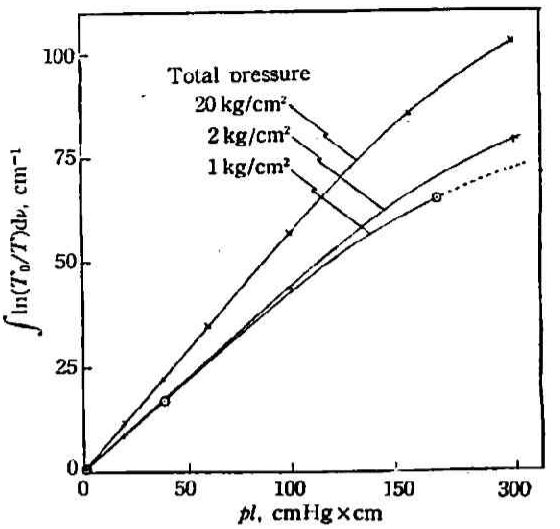

Fig. 6 The quantity $\int \ln(T_0/T)d\nu$ of 1328.1 cm^{-1} band of C_2H_2 pressurized with O_2 as the function pl

Table Infrared and Raman spectra of gaseous C_2H_2

Frequency cm^{-1}	Band type	Assignment	Reference
611.8	R. v. w.	ν_4	
729.1	I. ⊥ v. s.	ν_5	
1328.1	I. ∥ s.	$\nu_4+\nu_5$	
1956	I. ⊥ w.	$2\nu_4+\nu_5$	(9)
1973.8	R. v. s.	ν_2	(8)
2215	I. ∥ ? w.	$3\nu_5$?	
2701.5	I. ⊥ m.	$\nu_2+\nu_5$	
3287	I. ∥ v. s.	ν_3	
3294?	I. ∥ w.	$\nu_3+\nu_4+\nu_5$	
3373.7	R. s.	ν_1	
3881	I. ⊥ w.	$\nu_2+2\nu_4+\nu_5$	
3897	I. ⊥ m.	$\nu_3+\nu_4$	
4091	I. ⊥ m.	$\nu_1+\nu_5$	

The measuring gaseous acetylene contained the impurities of about 0.4 per cent.

8) G. Glockler and C. E. Morrel, *J. Chem. Phys.*, 4, 15 (1936)
9) F. Stitt, *ibid.*, 8, 56 (1940)

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in which the air as the main part, and traces of water vapour, hydrocarbons of paraffin (methane, ethane, propane etc.) and olefine (ethylene, propylene etc.), and hydrogen etc. might be contained. As the infrared absorption band locating at the frequency of about 1974 cm^{-1} can not be observed for these gaseous impurities, it is unlikely that the pressure-induced band at 1974 cm^{-1} is caused by the impurities.

Another pressure-induced absorption can be observed at the frequency range of 3287~3500 cm^{-1} for gaseous acetylene, although the band is not splitting from the very strong absorption band at 3287 cm^{-1} (ν_3).

The integrated absolute absorption coefficient A for unit pressure is defined by the equation

$$A=(1/pl)\int \ln(I_0/I)d\nu, \tag{1}$$

where I is the light transmitted through a cell of length l containing a gas at pressure p, and I_0 is the incident intensity, and the integration is carried out over the frequency range covered by a given band. The measurable quantity from which A is to be estimated is the integrated apparent absorption coefficient B for unit pressure

$$B=(1/pl)\int \ln(T_0/T)d\nu', \tag{2}$$

where T is the apparent intensity registered by the instrument when its setting is ν' (actual frequency ν), and T_0 is the apparent incident intensity. The value of B can be given as the slope of experimental curve showing the dependence of the quantity $\int \ln(T_0/T)d\nu'$ on the function of pl. According to E. B. Wilson and A. J. Wells, the limiting slope which is estimated by the extrapolation to zero partial pressure of the absorbing gas corresponds to the integrated absolute absorption coefficient, being given by the following equation.

$$\lim_{pl\to 0} B = A. \tag{3}$$

The addition of non-absorbing foreign gases at high pressure causes the increase of the integrated absolute absorption coefficient (Fig. 6). The fact is ascribed to the pressure broadening of the individual rotational lines of the band combined with the finite spectral resolution of the instrument. Such pressure broadening is attributed to the fact that the surrounding foreign gas molecules at high density induce the dipole in the absorbing molecules, additively to the original dipole. The integrated absolute absorption coefficient of the free absorbing gas can be given by the extrapolation of the linear variation of the absolute absorption coefficient in the gaseous mixture with the Amagat density of the foreign gas to zero density of the foreign gas.

The author has great pleasure in expressing his sincere thanks to Prof. R. Kiyama for his advice and encouragement throughout the course of this investigation. He is also partly indebted to the Department of Education for the Grant in Aid for Fundamental Scientific Research.

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